

REC'D 0 8 JUL 2004

WIPO

PCT

# ANIOR UNIVERDISHAMES OF AMERICA

TO AND TO WHOM THESE: PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE United States Patent and Trademark Office

July 02, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/461,642

FILING DATE: April 09, 2003

P1 1189429

RELATED PCT APPLICATION NUMBER: PCT/US04/10837

By Authority of the

COMMISSIONER OF PATENTS AND TRADEMARKS

N. WOODSON
Certifying Officer

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)



Approval for use through OMB 0651-00-XX

Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE

### PROVISIONAL APPLICATION COVER SHEET

request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

•								N. CO	
	Docket Number			62620	Type a plus inside thi	sign (+) is box	7/0		
·	INVE	NTOR(s)/A	PPLICA	ANT(s)		•		<u> </u>	
1 LAST NAME	FIRST NAME		MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FORE COUNTRY)				eign	
Pyzik Hu - Morgan Lister	Aleksander Terry Ted Daniel		J. I. A. R.	Midland, Michigan Midland, Michigan Midland, Michigan Midland, Michigan					
** Additional inventors	। s are being nam	ed on sepai	 ratelv nui	nhered	Sh <i>oo</i> ts atta	sohod havetaki	<b>.</b>		
<u>TI</u>	TLE OF THE	INVENTI	ON (280	charac	ters may	cneu nereto			
	MPOSITION FOR								
		SPONDE							
THE DOW CHEMICAL COMPANY Intellectual Property P. O. Box 1967 Midland, MI 48641-1967 U.S.A.			Telephone: 989-636-2540 Fax: 989-636-3237					_	
ENCL	OSED APPLIC	CATION F	PARTS (	check a	ll that an	nlv)		•	
Specification Number of Pages 12			☐ Small Entity Statement						
Drawing(s) Number of Sheets 1				Other (specify)					
<u> </u>	METHOD	OF PAYN	IENT (c	heck on	ie) ·			<del></del>	
A check or money order is enclosed to cover the Provisional filing fees  The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number:  04-1512				PROVISIONAL FILING FEE \$16 AMOUNT			0.00		
The invention was made by an agency of No  Yes, the name of the U.S. Gov						ey of the United S	States Gov	ernment	
Respectfully submitted,			Col	idact hun	noer are:				
Timothy 5, 8ten	On.		EXPRE DATE (	SS MAIL	MAILING	NO.: EV 2540	066941 U	S	

Timothy Stevens

Registration No.:

32,441

Phone No.:

(989) 839-9296

TS/blw

PROVISIONAL APPLICATION FILING ONLY

## COMPOSITION FOR MAKING METAL MATRIX COMPOSITES

#### 5 BACKGROUND

10

15

20

25

30

Metal Matrix Composites (MMC) are a class of materials wherein a reinforcing filler is interdispersed with a metal phase. See Rohatgi, Defence Science Journal, Vol. 43, No. 4, October 1993, pp 323-349. In the preparation of one type of MMC material, particulate ceramic reinforcing filler is mixed with a molten metal and then the mixture is cooled to form an MMC article. In the preparation of another type of MMC material, a porous ceramic preform comprising a ceramic reinforcing filler is infiltrated with a molten metal and then the metal-filled preform is cooled to form the MMC article. MMC's tend to be stiffer and stronger than metals but more ductile than ceramics.

In general, in order to achieve high performance in an MMC made by mixing a ceramic reinforcing filler with a molten metal and then cooling the mixture to form the MMC article, there should be: (a) good wettability of the ceramic reinforcing filler by the molten metal; (b) good chemical stability of the ceramic reinforcing filler in the molten metal; (c) good dispersion of the ceramic reinforcing filler in the molten metal; and (d) good adhesion between the ceramic reinforcing filler and the metal after the MMC is formed.

In general, in order to achieve high performance in an MMC made by wetting a preform with a molten metal and then cooling the metal-filled preform to form an MMC article, there should be: (a) good wettability of the ceramic reinforcing filler of the preform by the molten metal; and (b) good adhesion between the ceramic reinforcing filler and the metal after MMC is formed.

Ceramic reinforcing fillers that perform well in MMC's (for example, titanium diboride or titanium carbide mixed with molten aluminum or porous boron carbide preforms infiltrated with molten aluminum) are relatively expensive resulting in significantly increased cost of an MMC article. Ceramic reinforcing fillers that are relatively low in cost tend to perform poorly in MMC's. For example, alumina  $(\mathrm{Al}_2\mathrm{O}_3)$  and silica  $(\mathrm{SiO}_2)$  are relatively low cost materials but neither silica nor alumina are wetted by molten aluminum. Alumina reinforcing filler particles tend to agglomerate in molten aluminum instead of being well dispersed while silica reacts in molten aluminum to form Si rich Al and  $Al_2O_3$ . It would be a substantial advance in the MMC art if the relatively low cost ceramic reinforcing fillers of the type that are not wetted by molten aluminum could be used to produce lower cost, high performance MMC's.

### SUMMARY OF THE INVENTION .

The instant invention is a solution, at least in part, to the above stated problem. In the instant invention, low 20 cost/poor performance ceramic reinforcing fillers are converted into low cost/high performance materials by coating with a ceramic material that is wettable by and/or chemically stable in molten aluminum, molten magnesium, molten copper, molten titanium or alloys thereof. More 25 specifically, the instant invention is a composition to be mixed with a molten metal to make a metal matrix composite or to make a porous preform to be infiltrated by a molten metal to make a metal matrix composite, the composition comprising: ceramic reinforcing filler, the ceramic 30 reinforcing filler not being wettable by molten aluminum and/or not being chemically stable in molten aluminum, the ceramic reinforcing filler being coated with a ceramic material, the ceramic material being wettable by and/or chemically stable in molten aluminum, molten magnesium, 35

10

molten copper, molten titanium or alloys thereof. The surface of such coated ceramic reinforcing filler can additionally be coated with a metal, such as nickel or tungsten. The instant invention also includes matrix metal composite articles made using such compositions such as motor vehicle parts.

### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view of a composition of the instant invention consisting of an alumina particle coated with a layer of boron carbide; and

Fig. 2 is a cross-sectional view of another composition of the instant invention consisting of a silica particle coated with a layer of titanium diboride that is in turn coated with a layer of nickel.

### DETAILED DESCRIPTION OF THE INVENTION .

sectional view of a composition 10 of the instant invention consisting of an alumina reinforcing filler particle 12 coated with a layer of boron carbide 12. The layer of boron carbide 12 is formed on the alumina particle 12 by plasma sputtering boron carbide onto mechanically stirred alumina particles in a conventional plasma-sputtering chamber. Uncoated alumina particles are not "wetted" by molten aluminum. The term wetted as used herein means a contact angle greater than ninety degrees. The boron carbide coating is wetted by molten aluminum, e.g., aluminum at a temperature above 1000 degrees Centigrade.

The embodiment shown in Fig. 1 can be formed into a porous ceramic preform by any suitable technique (such as slip casting), contacting the porous preform with molten aluminum followed by cooling to form an MMC article. The molten aluminum will wick into the porous preform because

molten aluminum wets the boron carbide layer 11 on the alumina particle 12.

The embodiment shown in Fig. 1 is not specifically suitable for mixing with molten aluminum for casting MMC articles because the boron carbide layer 11 tends to react with the molten aluminum before the molten aluminum can be cast, i.e., the boron carbide layer is not chemically stable in the molten aluminum and the resulting de-coated alumina particles then tend to agglomerate in the molten aluminum. Thus, when alumina reinforcing filler is used in the instant invention for mixing with molten aluminum for casting MMC articles, a chemically stable ceramic material coating is used such as titanium diboride or more preferably titanium diboride additionally coated with tungsten or nickel. Similarly, when a graphite reinforcing filler is used, the ceramic material coating can be silicon carbide or titanium diboride that is more preferably additionally coated with tungsten, cobalt or nickel.

Referring now to Fig. 2, therein is shown a cross-sectional view of another composition 20 of the instant invention that is highly preferred consisting of a silica reinforcing filler particle 23 coated with a layer of titanium diboride 22 that is in turn coated with a layer of nickel 21. The layer of titanium diboride 22 is wetted by molten aluminum but the layer of nickel 21 enhances the wettability of the composition 21 with molten aluminum. The layer of titanium diboride 22 is formed on the silica particle 23 by plasma sputtering titanium diboride onto mechanically stirred silica particles in a conventional plasma-sputtering chamber. The layer of nickel 21 is then formed by conventional electroless nickel coating.

The embodiment shown in Fig. 2 is specifically suitable for mixing with molten aluminum for casting MMC articles because the titanium diboride layer 22 does not react with

10

15

20

the molten aluminum (even in the absence of the nickel layer 21) before the molten aluminum can be cast, i.e., the titanium diboride layer 22 is chemically stable in molten aluminum.

The discussion above related to Figs 1 and 2 is directed to specific embodiments. However, it should be understood that in its broad scope, the instant invention is a composition to be mixed with a molten metal to make a metal matrix composite or to make a porous preform to be 10 infiltrated by a molten metal to make a metal matrix composite, the composition comprising: ceramic reinforcing filler, the ceramic reinforcing filler not being wettable by molten aluminum and/or not being chemically stable in molten aluminum, the ceramic reinforcing filler being coated with a ceramic material, the ceramic material being wettable by and/or chemically stable in molten aluminum, molten magnesium, molten copper, molten titanium or alloys thereof.

The ceramic reinforcing filler is preferably selected from the group consisting of oxides, carbides, borides and nitrides such as sand, clay, mullite, alumina, titanium dioxide, magnesium oxide, silica, carbon, iron oxide, yttrium oxide, zirconium oxide, molybdenum oxide, tantalum oxide, niobium carbide, tungsten carbide and silicon The ceramic reinforcing filler is most preferably selected from the group consisting of alumina, silicon carbide, silica and acicular mullite. The ceramic material coating is preferably selected from the group consisting of titanium diboride, aluminum nitride, titanium nitride, titanium carbide, silicon carbide and boron carbide. optional additional metal coating is preferably selected from group consisting of W, Mo, Ti, Ni, Cu, Hf, Fe, Co, Al and Si. The ceramic material can be coated onto the ceramic reinforcing filler by any suitable method but preferably by conventional plasma sputtering. Most preferably, the metal

15

20

25

optionally coated on the ceramic material coating is nickel or tungsten. The metal layer can be coated onto the ceramic material layer by any suitable method such as electroless deposition, electroplating and plasma sputtering.

Acicular mullite coated with titanium diboride is a preferred embodiment of the instant invention. Acicular mullite coated with titanium diboride and then coated with nickel is also a preferred embodiment of the instant invention. Carbon (amorphous or graphitic carbon) coated with silicon carbide is a preferred embodiment of the instant invention. Carbon (amorphous or graphitic carbon) coated with silicon carbide and then coated with tungsten, copper or nickel is also a preferred embodiment of the instant invention. The ceramic reinforcing filler can be of any shape, e.g., in the shape of platelets, whiskers or fibers as well as particles having an aspect ratio closer to or equal to one.

The thickness of the coating of ceramic material on the ceramic reinforcing filler is preferably less than one micrometer, more preferably less than one half micrometer, and even more preferably less than one tenth of one micrometer. A thinner coating is preferred to reduce the cost of the composition. However, a coating of ceramic material that is too thin will leave a sufficient portion of the filler exposed to the molten metal resulting in chemical instability of the filler and/or agglomeration of the filler. Most preferably, the coating is both thin and completely covers the filler.

Metal matrix composite articles of the instant invention can be made from the compositions of the instant invention by: (a) mixing a molten metal, such as molten aluminum or molten aluminum alloy, with such a composition to form a metal-composition mixture; and (b) then cooling the metal-composition mixture to form the metal matrix

10

15

20

composite article. In most cases, the metal-composition mixture will be introduced into a mold before step (b).

Metal matrix composite articles of the instant invention can also be made from the compositions of the instant invention by: (a) forming a porous perform, the porous perform comprising such a composition; (b) infiltrating the porous perform with molten metal, such as molten aluminum or molten aluminum alloy, to form an infiltrated perform; and (c) cooling the infiltrated perform to form the metal matrix composite article. For example, the perform can comprise interconnected mullite grains having a needle morphology (acicular mullite) as the ceramic reinforcing filler.

The metal matrix composite articles of the instant invention can be used in an almost unlimited number of 15 applications. For example, the metal matrix composite article of the instant invention can be a thermal management article selected from the group consisting of heat spreaders, heat sinks, combination heat spreaders/heat sinks and thermal base plates. Examples of metal matrix composite 20 articles of the instant invention for motor vehicle application include parts selected from the group consisting of disk brake rotors, brake pads, brake pistons, brake calipers, brake pad back plates, brake drums, steering knuckles, engine cylinder liners, cylinder head inserts, pistons, piston rings, main bearing inserts, cam lobes, cam followers, valves, valve guides and valve seats.

#### WHAT IS CLAIMED IS:

10

- 1. A composition to be mixed with a molten metal to make a metal matrix composite or to make a porous preform to be infiltrated by a molten metal to make a metal matrix composite, the composition comprising: ceramic reinforcing filler, the ceramic reinforcing filler not being wettable by molten aluminum and/or not being chemically stable in molten aluminum, the ceramic reinforcing filler being coated with a ceramic material, the ceramic material being wettable by and/or chemically stable in molten aluminum, molten magnesium, molten copper, molten titanium or alloys thereof.
- 2. The composition of Claim 1, further comprising a layer of a metal coated on the ceramic material.
- 3. The composition of Claim 1, wherein the ceramic
  reinforcing filler is selected from the group consisting of
  filler comprising oxides, carbides, borides, silicides and
  nitrides.
- The composition of Claim 2, wherein the ceramic reinforcing filler is selected from the group consisting of
   filler comprising oxides, carbides, borides, silicides and nitrides.
  - 5. The composition of Claim 1, wherein the ceramic reinforcing filler is selected from the group consisting of filler comprising of sand, clay, mullite, alumina, titanium dioxide, magnesium oxide, silica, carbon, iron oxide, yttrium oxide, zirconium oxide, molybdenum oxide, tantalum oxide, niobium carbide, tungsten carbide and silicon carbide.
- 6. The composition of Claim 2, wherein the ceramic reinforcing filler is selected from the group consisting of filler comprising of sand, clay, mullite, alumina, titanium dioxide, magnesium oxide, silica, carbon, iron oxide, yttrium oxide, zirconium oxide, molybdenum oxide, tantalum

oxide, niobium carbide, tungsten carbide and silicon carbide.

- 7. The composition of Claim 3, wherein the ceramic material coated on the ceramic reinforcing filler is selected from the group consisting of titanium diboride, aluminum nitride, aluminum oxide, titanium nitride, titanium carbide, silicon carbide and boron carbide.
- 8. The composition of Claim 4, wherein the ceramic material coated on the ceramic reinforcing filler is selected from the group consisting of titanium diboride, aluminum nitride, aluminum oxide, titanium nitride, titanium carbide, silicon carbide and boron carbide.
  - 9. The composition of Claim 1, wherein the composition comprises aluminum oxide coated with titanium diboride.
- 15 10. The composition of Claim 2, wherein the composition comprises aluminum oxide coated with titanium diboride and then further coated with nickel.
  - 11. The composition of Claim 1, wherein the ceramic reinforcing filler comprises mullite and wherein the ceramic material comprises titanium diboride.
  - 12. The composition of Claim 2, wherein the ceramic reinforcing filler comprises mullite, wherein the ceramic material comprises titanium diboride and wherein the metal comprises nickel.
- 25 13. The composition of Claim 2, wherein the ceramic reinforcing filler comprises carbon, wherein the ceramic material comprises silicon carbide and wherein the metal comprises copper.
- 14. The composition of Claim 2, wherein the ceramic reinforcing filler comprises carbon, wherein the ceramic material comprises silicon carbide and wherein the metal comprises nickel.

- 15. The composition of Claim 1, wherein the ceramic reinforcing filler comprises carbon and wherein the ceramic material comprises titanium carbide.
- 16. The composition of Claim 2, wherein the metal is selected from the group consisting of nickel, tungsten, aluminum and copper.
  - 17. The composition of Claim 1, wherein the ceramic reinforcing filler comprises carbon and wherein the ceramic material comprises tungsten carbide.
- 10 18. The composition of any of Claims 1-17, wherein the ceramic reinforcing filler has a shape selected from the group consisting of particles, platelets, whiskers and fibers.
  - 19. A metal matrix composite article made by a process
    comprising the steps of: (a) mixing a molten metal with the composition of any of Claims 1-18 to form a metalcomposition mixture; and (b) cooling the metal-composition mixture to form the metal matrix composite article.
  - 20. The metal matrix composite article of Claim 19, further comprising the step of filling a mold with the mixture of step (a) before step (b).
    - 21. A metal matrix composite article made by a process comprising the steps of: (a) forming a porous perform, the porous perform comprising the composition of any of Claims
  - 25 1-18; (b) infiltrating the porous perform with molten metal to form an infiltrated perform; and (c) cooling the infiltrated perform to form the metal matrix composite article.
  - 22. The metal matrix composite article of Claim 21; wherein the perform comprises acicular mullite.
    - 23. The metal matrix composite article of any of Claims 19-22, wherein the article is a thermal management article selected from the group consisting of heat spreaders, heat

sinks, combination heat spreaders/heat sinks and thermal base plates.

- 24. The metal matrix composite article of any of Claims 19-22, wherein the article is a motor vehicle part selected
- from the group consisting of disk brake rotors, brake pads, brake pistons, brake calipers, brake pad back plates, brake drums, steering knuckles, engine cylinder liners, cylinder head inserts, pistons, piston rings, main bearing inserts, cam lobes, cam followers, valves, valve guides and valve
- 10 seats.

#### ABSTRACT OF THE DISCLOSURE

A composition to be mixed with a molten metal to make a metal matrix composite or to make a porous preform to be infiltrated by a molten metal to make a metal matrix composite. The composition consists of ceramic reinforcing filler particles that are not wettable by molten aluminum and/or are not chemically stable in molten aluminum, the ceramic reinforcing filler particles being coated with a ceramic material that is wettable and/or chemically stable in molten aluminum, molten magnesium, molten copper or molten titanium. The instant invention also includes matrix metal composite articles made using such compositions such as motor vehicle parts.

COMPOSITIONS FOR MAKING METAL
MATRIX COMPOSITES
Pyzik, et al.
62620

Sheet 1 of 1

## FIG. 1

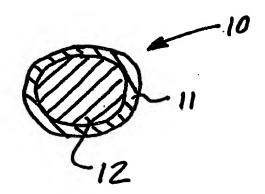


FIG. 2

